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## EUROPEAN PATENT APPLICATION

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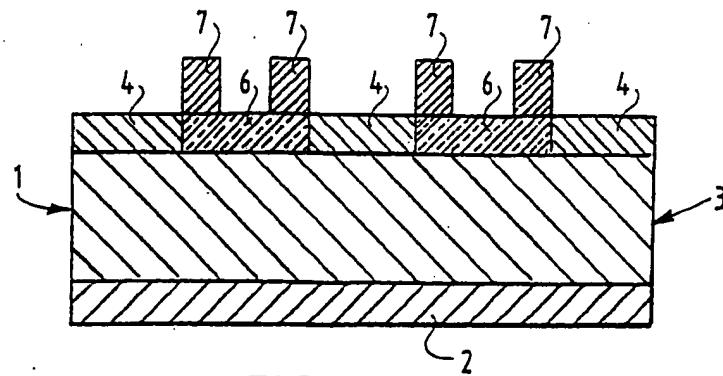
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### ⑯ Sensor of the diode type

⑰ Sensor of the diode type for sensing to what extent one or more gases are present, comprising: a semiconducting substrate of a first conductivity type which is provided with a contact electrode; a layer of

semiconducting material of the other conductivity type, wherein a heterojunction is formed between the substrate and the layer; and one or more contact parts arranged on this layer.



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There is a world-wide search under way for sensitive and rapidly responding sensors for sensing the presence of one or more gases (or vapours and the like). Such a sensor is disclosed in the European patent application EP-A2-299780.

The present invention has for its object to provide a new sensor, wherein a heterojunction is used for sensing to what extent one or more gases are present.

The present invention provides a sensor as according to claim 1.

First results have shown that such a sensor already displays a degree of sensitivity adequate for practical purposes at temperatures in the vicinity of ambient temperature.

The present invention further provides a method for manufacturing such a sensor.

Further advantages, features and details of the present invention will be elucidated in the light of a description of a preferred embodiment thereof, wherein reference is made to the annexed drawing, in which:

Fig. 1 shows a view in section of a preferred embodiment of a sensor according to the present invention;

fig. 2A-2G show schematic views in section of the successive method steps for manufacturing the preferred embodiment of fig. 1; and

fig. 3 shows a graph of a measured characteristic of the preferred embodiment of fig. 1.

The preferred embodiment shown in fig. 1 of a sensor 1 according to the present invention comprises a contact electrode 2 preferably of aluminium (or another conducting material such as gold) which is arranged beneath a P-type Si-substrate 3 onto which, between regions 4 of insulating material such as  $\text{SiO}_2$  (or another insulator such as  $\text{Si}_3\text{N}_4$ ), are applied Sn regions 6 of  $\text{SnO}_2$ , above which are arranged electrodes or contact parts 7 of finger shape, preferably of Pd (Palladium) or another metal or conducting semiconductor material which in preference has catalytic properties and makes good contact with  $\text{SnO}_2$ .

The material  $\text{SnO}_2$  is an N-type semiconductor with a large band gap (3.4 eV). The metal, preferably Pd, has a catalytic effect on the gas for sensing from which hydrogen atoms are released which penetrate into the  $\text{SnO}_2$ . If hydrogen atoms enter the  $\text{SnO}_2$ , conducting electrons are released therein, whereby conduction increases, or the contact potential between  $\text{SnO}_2$  and the P-type substrate. This phenomenon will already occur at a comparatively low temperature such as room temperature (300K).

The sensor 1 is preferably manufactured in the following manner:

- to a P-type substrate 10 (fig. 2A) with a band gap of about 1.1 eV (resistivity 1-10  $\Omega\text{cm}$ )

provided with a layer of insulating material 11 is applied a layer of photoresist 12 (fig. 2B) whereafter using a mask 13 a portion of the photoresist is illuminated and exposed parts of the  $\text{SiO}$  are etched away (fig. 2C);

- a layer of tin (Sn) is then sputtered thereon. After removal of the remaining photoresist and tin by means of a lift-off process and thermal treatment in an oxygen-containing environment, there results an  $\text{SnO}_2$  region 14 (fig. 2D);

- a layer of photoresist 15 (fig. 2E) is subsequently applied over the structure, whereafter, following illumination with a mask 16 (fig. 2F) and subsequent developing, the pattern is created for the vapour deposition of the finger-shaped Pd structure 17 (fig. 2G), wherein a contact part 18 of Al (aluminium) is arranged at the rear.

The measured voltage characteristic of the diode structure of fig. 1 and 2 in relation to the current is shown in fig. 3, in which the curve  $C_1$  indicates the characteristic in air while the curve  $C_2$  is measured in a hydrogen environment, both at 50°C.

It has been determined experimentally that the diode characteristic is caused by the heterojunction between P-type Si and the N-type  $\text{SnO}_2$ .

It has also been demonstrated experimentally that the measured values are sufficiently independent of the ambient temperature to perform sufficiently sensitive measurements on the concentration of the gases present.

The present invention is not limited to the embodiment described. Other possible materials with a large band gap are  $\text{In}_2\text{O}_3$ ,  $\text{InT}_2\text{O}$ ,  $\text{InSb}$  and ITO, wherein particularly ITO (indium tin-oxide) has the further advantage that it is transparent for visible light and displays a screening action for infrared radiation. Nor is the present invention limited to the described method for applying the  $\text{SnO}_2$  regions:

- $\text{SnO}_2$  can be applied by means of CVD techniques (gas phase) or using sol-gel techniques, or by means of reactive sputtering or vapour deposition.
- instead of using the lift-off process, tin deposition can take place via vapour deposition or sputtering followed by thermal oxidation.

## Claims

1. Sensor of the diode type for sensing to what extent one or more gases are present, comprising:

- a semiconducting substrate of a first conductivity type which is provided with a contact electrode;

- a layer of semiconducting material of the other conductivity type, wherein a heterojunction is formed between the substrate and the layer; and
- one or more contact parts arranged on this layer.

2. Sensor as claimed in claim 1, wherein the semiconductor substrate comprises P-type Si and the semiconducting layer comprises material from the group  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{InT}_2\text{O}$  and  $\text{InSb}$ .

3. Sensor as claimed in claim 1 or 2, wherein the contact parts are formed from Pd.

4. Method for manufacturing the sensor as claimed in any of the claims 1-3.

5. Method as claimed in claim 4, wherein the layer of semiconducting material is formed by sputtering oxidized metal, preferably Sn, onto the substrate.

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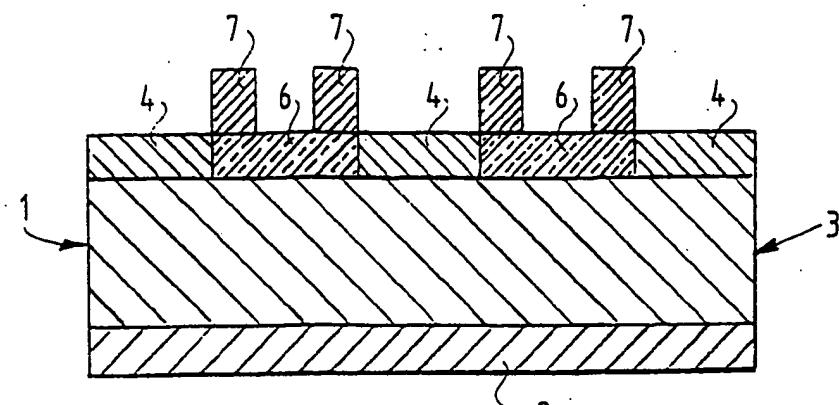


FIG.1

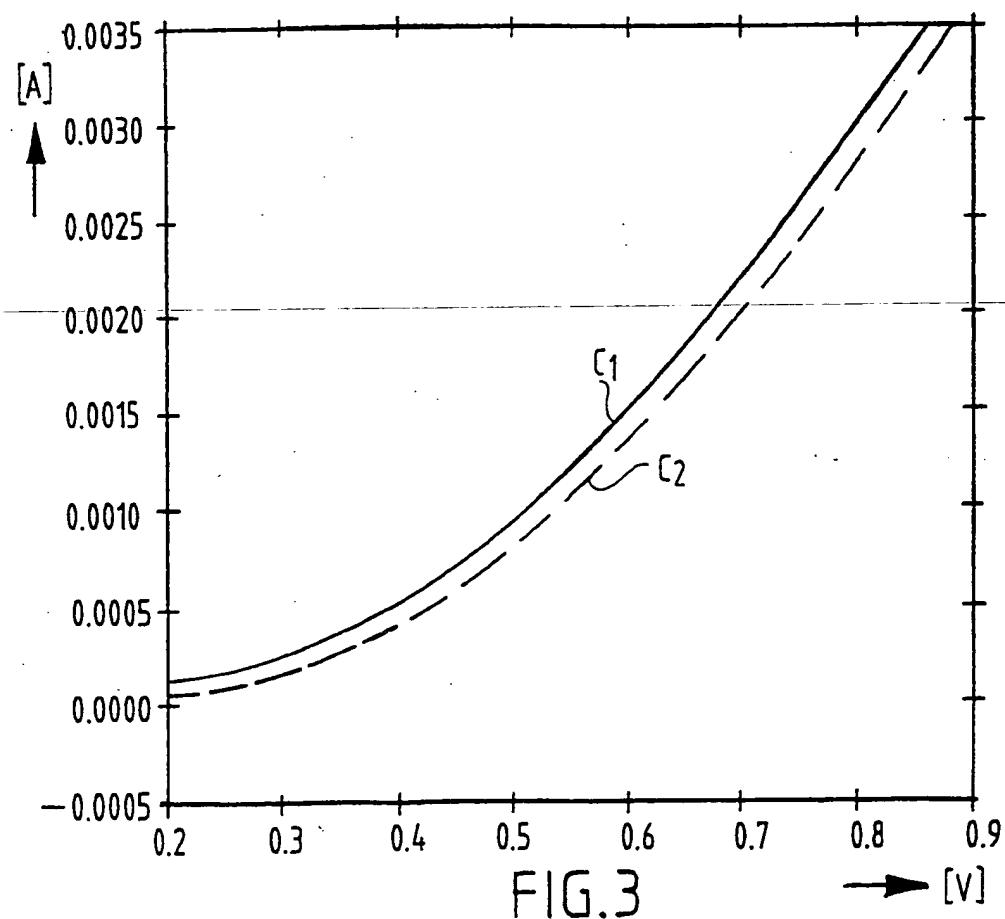


FIG.3

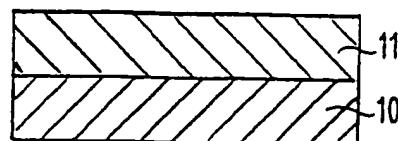


FIG. 2a

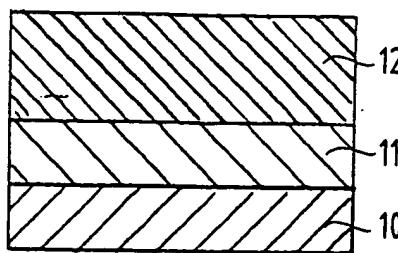


FIG. 2b

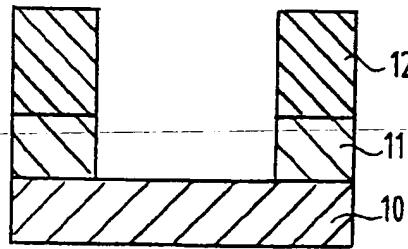


FIG. 2c

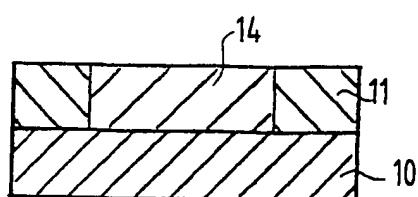


FIG. 2d

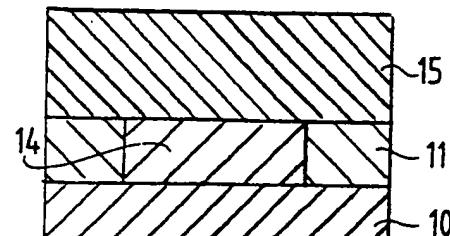


FIG. 2e

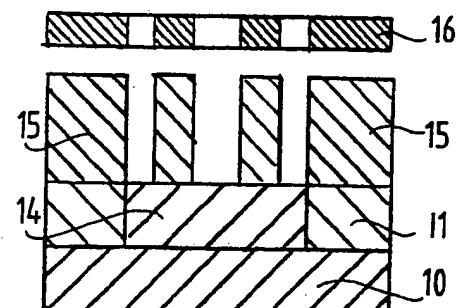


FIG. 2f

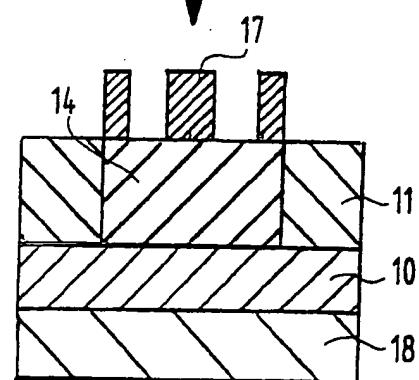


FIG. 2g



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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	US-A-4 001 756 (HEIJNE) * column 2, line 63 - column 3, line 28 * * column 4, line 22 - column 4, line 45; figures 1,2 * —	1-4	G01N27/414 G01N27/12
Y	JAPANESE JOURNAL OF APPLIED PHYSICS. vol. 20, no. 10, October 1981, TOKYO JP pages 753 - 756; K. ITO: 'HYDROGEN DETECTOR UTILIZING METAL-SEMICONDUCTOR CONTACTS' * page 753, right column, paragraph 3 - page 754, left column, paragraph 2; figure 1 *	1-4	
Y	US-A-2 975 362 (JACOBSON) * column 2, line 55 - column 3, line 46 * * column 7, line 26 - column 8, line 16; figures 8-14 *	1-4	
A	US-A-4 103 227 (ZEMEL) * column 2, line 50 - column 3, line 39; figure 2 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	IEEE TRANSACTIONS ON ELECTRON DEVICES, vol. ED-29, no. 1, January 1982, NEW YORK US pages 123 - 129; T.L. POTEAT ET AL.: 'TRANSITION METAL-GATE MOS GASEOUS DETECTORS' * page 124, left column, paragraph 5 - page 125, left column, paragraph 2; figure 1A *	1-3	
A	US-A-4 058 368 (SVENSSON) * column 2, line 1 - line 27; figures 1,2 *	1-3	
A	EP-A-0 203 561 (SIEMENS) * page 11, paragraph 7 - page 12, paragraph 1; figure 1 *	1-3	
		—/—	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	06 APRIL 1992	R.A.P. BOSMA	
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	DE-A-2 535 500 (NISSAN) * page 5, paragraph 2 * * page 6, paragraph 3 - page 7, paragraph 2; figure 1 *	1, 2	
A	EP-A-0 397 576 (TERUMO K.K.) * page 2, line 44 - line 48 * * abstract *	2	
TECHNICAL FIELDS SEARCHED (Int. CL.5)			
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 06 APRIL 1992	Examiner R. A. P. BOSMA	
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